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On the Existence of Intercalation Compound of Boron Nitride with Ferric Chloride

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Mössbauer effect and X-ray diffraction measurements were made in order to clear up the ambiguity on the existence of intercalation compound of BN with FeCl_3 . The present work confirmed that the intercalation did not occur when the mixture of BN and FeCl_3 was heated in a sealed tube, independently of temperatures (280–450°C) and durations (1–5 days). Under a certain condition, pink specimens were obtained which were the same ones as those produced by Freeman and Larkindale. However, these were proved to be the hydrolysis product, FeOCl , by the Mössbauer and X-ray measurements.

INTRODUCTION

Some intercalation compounds of graphite are well known and their properties have been extensively investigated.¹⁾ The similarity of the structures of graphite and boron nitride led some workers to attempt the preparation of BN intercalation compounds. However, because of the difficulty in preparation and identifying them, their existence remains still ambiguous. The authors attempted to produce an intercalation compound of BN with FeCl_3 and the materials obtained were characterized with X-ray and Mössbauer measurements. Concerning the attempts to produce this intercalation compound, some works were already reported but the results were not consistent.

Croft²⁾ reported that BN formed "intercalation compounds" with a variety of molecules such as FeCl_3 . The main evidence for intercalation found by Croft was exfoliation occurring when particles of these compounds were heated in air. On the other hand, Rüdorff and Stumpp³⁾ did not find any evidence of intercalation in the preparation of BN- FeCl_3 compound, which led them to deny the existence of such an intercalation compound. These works used a white form of boron nitride and they attributed Croft's success to using an unusual black form. The black and lustrous boron nitride would probably contain a certain quantity of graphite, since graphite-crucibles were used in the process.

On the contrary, Freeman and Larkindale⁴⁾ reported that an evidence was obtained which a white powder of boron nitride formed a pink intercalation compound with FeCl_3 . They measured X-ray powder diffraction patterns of the products with low-angle X-ray reflections, and Mössbauer spectra with a fairly great quadrupole splitting ($\Delta E_Q = 0.93$ mm/sec at 298 K). They concluded that Rüdorff-Stumpp's failure of intercalation was due to low crystallinity and due to the small size of boron nitride particles. Mössbauer measurements were made only at room temperature. Their results are not sufficient to characterize the intercalation compound unambiguously. We have attempted to reproduce

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their results by using white boron nitride in order to obtain conclusive results on the existence of BN-FeCl₃ compound.

EXPERIMENTAL

The following two kinds of BN were used as the starting materials in the present work. (i) White powder (1–5 micron) provided by Mitsuwa Pure Chemical Co. Ltd., which had the following quoted analytical figures; B, 43.9, N, 55.6, and Fe < 0.001%. (ii) White rectangular plates (2.54×1.27 cm²) of pyrolytic BN provided by Union Carbide Corp. The boron nitride had the analytical figure B+N=99.99%. The mosaic spread in the *c*-axis alignment was determined from the full width at half-maximum, FWHM, of (00.2) CuK α reflection. The value of FWHM of pyrolytic BN was 2°. The crystallite thickness along the *c*-axis was determined from the line broadening. The value of thickness was 500–1000 Å for the pyrolytic BN, and >1000 Å for the white powder.

For most of tests, commercial-grade anhydrous FeCl₃ was used after purification by sublimation. For the convenience of Mössbauer spectroscopy some of the samples were prepared using ⁵⁷Fe isotope. Ferric oxide Fe₂O₃, including 10% enriched ⁵⁷Fe, was dissolved in 6N HCl boiling solution. The cooled solution was kept at 3°C in a desiccator in order to obtain the crystal of FeCl₃·6H₂O. Five grams of FeCl₃·6H₂O was added to 20 ml SOCl₂. This thionyl chloride was purified by distilling from quinoline and boiled linseed oil. The FeCl₃ obtained was dried and used for the tests. The above treatments were repeatedly employed to obtain FeCl₃. This method was found to be useful to obtain FeCl₃ without loss of ⁵⁷Fe.

A Mössbauer effect analyzer, Elscint, AME-30 was used in combination with a multi-channel analyzer, Northern Scientific, NS-900. The source ⁵⁷Co in Cu was parabolically vibrated at room temperature. The mirror image spectra were folded by a computer, and the geometrical background was thus cancelled out in the spectra.

X-ray reflections were obtained with a Rigaku-Denki powder diffractometer using CuK α radiation, operating at 50 kV and 80 mA.

RESULTS AND DISCUSSION

The method to react FeCl₃ with BN adopted here was the same as in the previous works.²⁻⁴⁾ After sealing anhydrous FeCl₃ and BN in evacuated Pyrex glass tubes, the tubes were heated under various conditions, *i.e.* temperatures (280–450°C) and durations (1–5 days). The tubes were then opened and excess anhydride in the BN was washed off with a dilute HCl solution. The end point of washing was checked by use of 0.1 N ammonium thiocyanate solution. The boron nitride was then washed by distilled water and dried in an oven at 110°C. We could not find any detectable change in color, shape, and crystal structure of BN upon the above treatments. Moreover, Mössbauer spectroscopic measurements showed no appreciable absorption even with ⁵⁷Fe-enriched specimens, suggesting that the Fe-content of these samples were extremely small.

These results are in agreement with those of Rüdorff-Stumpp but not with those of Croft and Freeman-Larkindale. Croft's boron nitride was probably contaminated with graphite as suggested by Rüdorff-Stumpp. In order to interpret the inconsistency of the

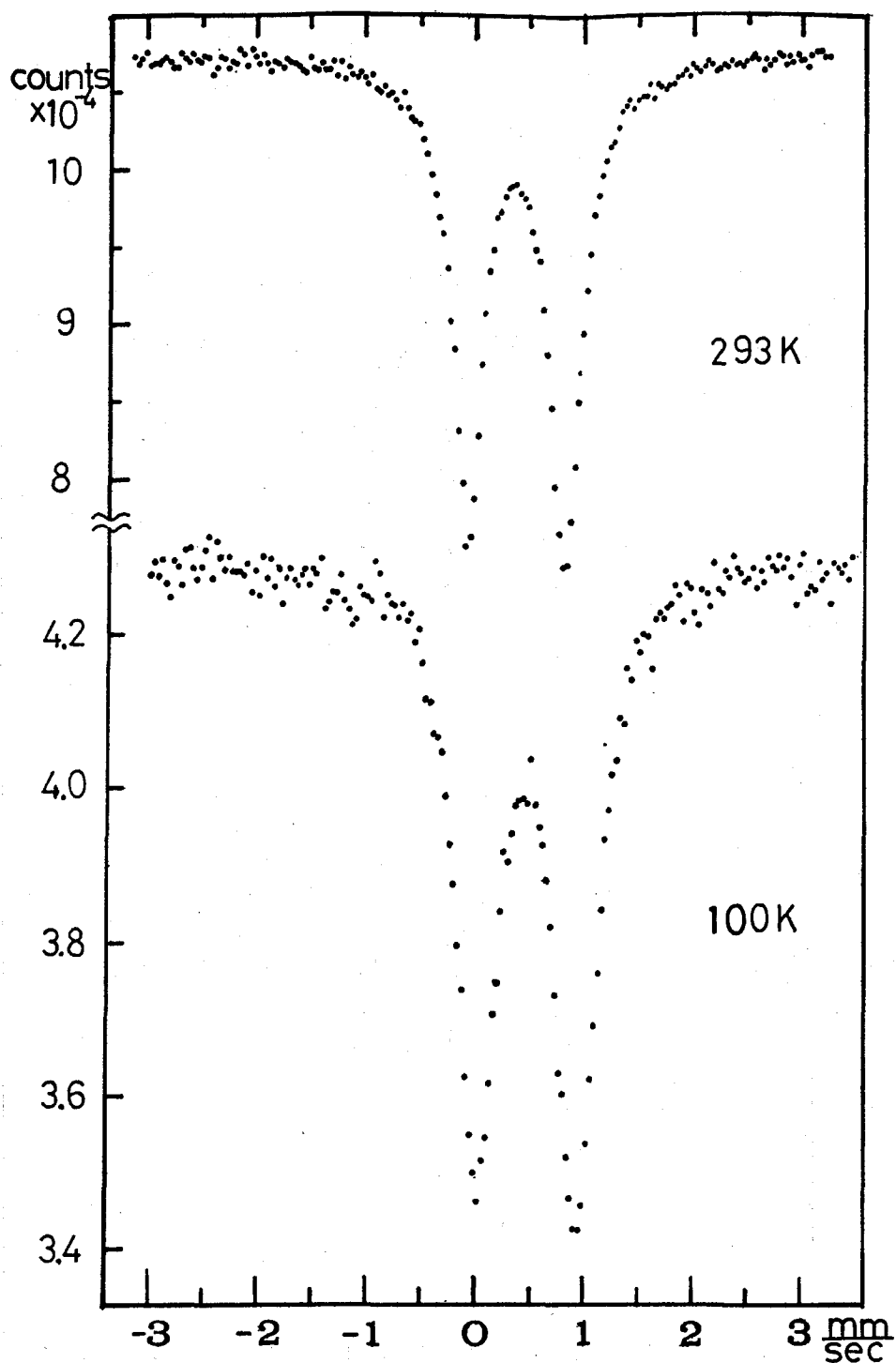


Fig. 1. Mössbauer absorption spectra of a pink specimen at 293K and 100K. The velocity scale is relative to iron metal at room temperature.

present work with Freeman-Larkindale's, we tried to search the condition to form a specimen with a pink color, which was considered as a characteristic of intercalation in Ref. 4. We found that a specimen showed a pink color when the mixture was heated in an open tube, or in a sealed tube with a certain quantity of water. On such a specimen, Mössbauer and X-ray measurements were carried out.

Mössbauer spectra were taken at 293 K, 100 K, 4.2 K, and 1.5 K. At 293 K and 100 K, the spectra were paramagnetic and the symmetric doublets due to a quadrupole interac-

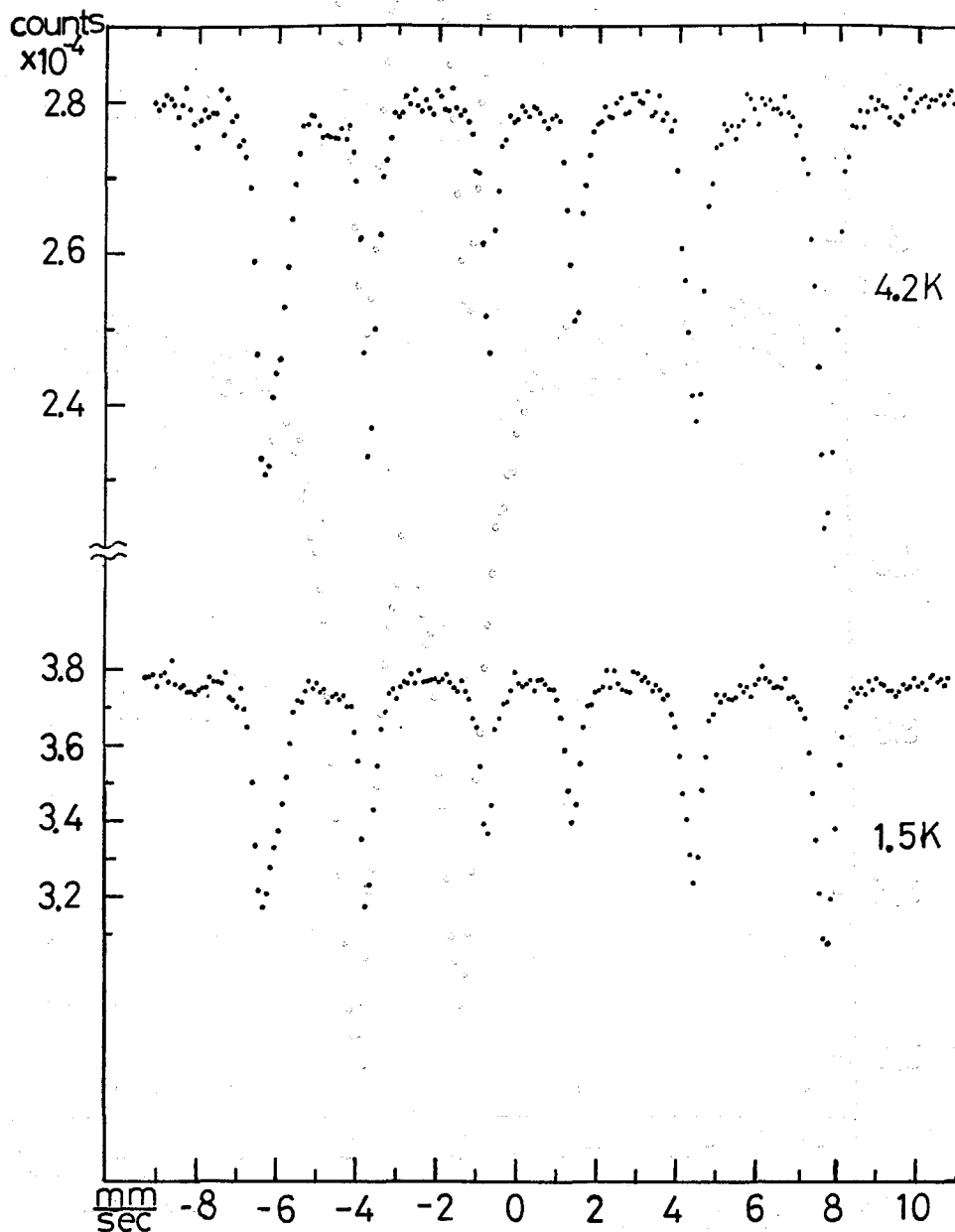


Fig. 2. Mössbauer spectra of the specimen at 4.2K and 1.5K.

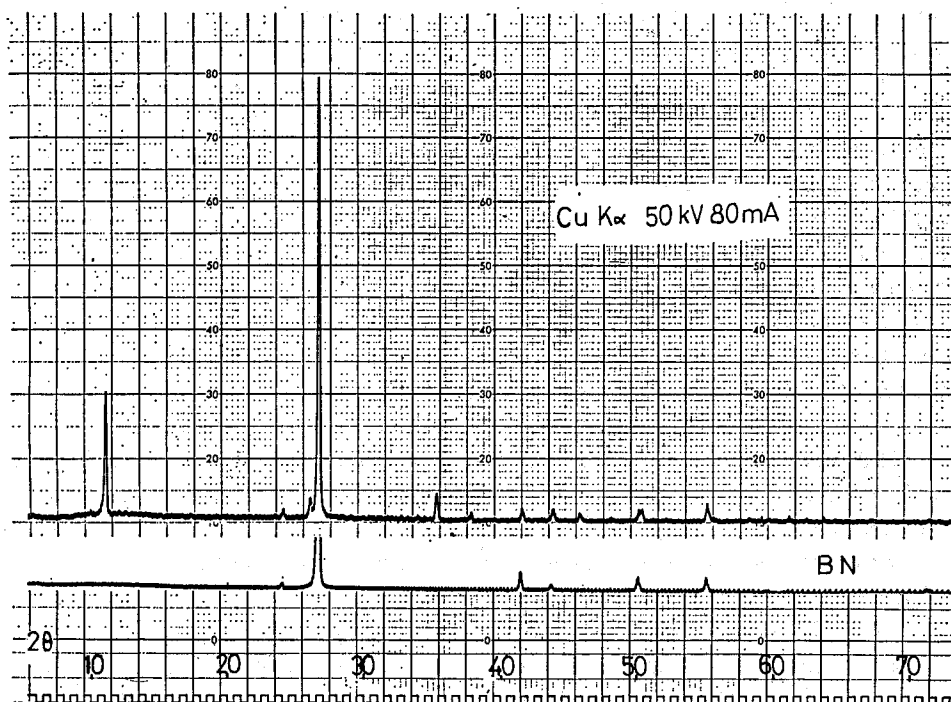


Fig. 3. X-ray diffraction pattern of the pink specimen and that of the starting boron nitride.

Table I.

d_{obs} (Å)	d_{cal} (Å)	BN (hkl)	FeOCl (hkl)
7.9	7.917		010
3.40	3.411		110
3.33	3.331	00.2	
2.53	2.536		021
2.37	2.373		111
2.17	2.169	10.0	
2.06	2.062		031
	2.061	10.1	
1.888	1.890		200
1.816	1.815	10.2	
1.807	1.810		131
1.663	1.665	00.4	
1.659	1.651		002
1.547	1.549	10.3	
1.513	1.515		221
1.485	1.486		112
1.252	1.252	11.0	
1.172	1.171	11.2	
1.108	1.110	00.6	

tion as shown in Fig. 1. The Mössbauer parameters at 293 K ($\delta=0.36$ mm/sec, $\Delta E_Q=0.90$ mm/sec) were in good agreement with Mössbauer data in Ref. 4. The spectrum at 100 K ($\delta=0.47$ mm/sec, $\Delta E_Q=0.90$ mm/sec) had broader line widths ($W_{1,2}=0.46$ mm/sec) than the one at 293 K ($W_{1,2}=0.34$ mm/sec). At 4.2 K and 1.5 K, the Mössbauer spectra given in Fig. 2 exhibited well resolved six lines with an internal field $H_i=437$ kOe. These are in good agreement with those for FeOCl, whose internal field was reported to be $H_i=430$ kOe.^{5,6)} The Néel temperature of FeOCl is 92 K. The spectra showed that only the outer-most line in the negative velocity side had a broad width. Such a profile is known to be a characteristic of FeOCl's spectra.

Figure 3 gives the X-ray diffraction pattern of a pink specimen as well as that of the starting boron nitride. The reflections could be assigned to BN and FeOCl. Table I summarizes the observed values, d_{obs} , the calculated ones, d_{cal} , as well as the assigned names of the planes. The values of d_{cal} were calculated based on the lattice constants; $a_0=2.504$ Å, $c_0=6.661$ Å for BN,⁷⁾ $a=3.780$ Å, $b=7.917$ Å, and $c=3.302$ Å for FeOCl.⁸⁾ It can be seen from Fig. 3 and Table I that the low-angle reflections are not due to intercalation but due to the mixing of FeOCl into BN.

Ferric oxychloride is known to be formed in the presence of water under the following reactions; (i) $2\text{FeCl}_3+3\text{H}_2\text{O}=6\text{HCl}+\text{Fe}_2\text{O}_3$, $\text{Fe}_2\text{O}_3+\text{FeCl}_3=3\text{FeOCl}$, (ii) $\text{FeCl}_3+\text{H}_2\text{O}=\text{FeOCl}+\text{HCl}$. Ferric chloride is easily washed out by a dilute HCl solution, but ferric oxychloride is not so easily. We could completely eliminate FeOCl mixed in BN by 6N HCl boiling solution. The hydrolysis process can probably be interpreted with the (ii) reaction in consideration of the small Fe-content in the form of Fe_2O_3 .

In conclusion, the intercalation did not occur when the mixture of BN and FeCl_3 was heated in a sealed tube, independently of temperatures (280–450°C) and durations (1–5 days). For other intercalation compounds of BN, further studies will be required to clear up the ambiguity of their existence.

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